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SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,  
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

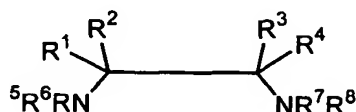
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ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.

(54) Title: IMMOBILISED LIGANDS DERIVED FROM ETHYLENEDIAMINE



(I)

(57) Abstract: An immobilised nitrogen-containing ligand is described comprising the reaction product of a compound of formula (I) wherein R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup> and R<sup>8</sup> are independently hydrogen, a saturated or unsaturated C1-C10 alkyl group, an aryl group, a urethane group, a sulphonyl group or form an imine group, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are independently hydrogen, a saturated or unsaturated C1-C10 alkyl group or an aryl group and at least one of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> is functionalised with a functional group, and a solid support having a site capable of reacting with said functional group. The nitrogen-containing ligand is useful for preparing immobilised catalysts for performing *e.g.* asymmetric catalysis.

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# INTERNATIONAL SEARCH REPORT

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PC.5/UB 03/03306

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J31/16 B01J31/18 C07B53/00 C07C29/136 C07C211/10  
C07C251/02 C07C209/42 C07C5/02 C07B37/04 C07D301/03  
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According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J C07B C07C C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EP0-Internal, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SONG C E ET AL: "Heterogenous asymmetric epoxidation of alkenes catalysed by a polymer-bound (pyrrolidine salen)manganese (III) complex" CHEMICAL COMMUNICATIONS, no. 7, 2000, pages 615-616, XP002265072 the whole document	1,4-6,8, 10,15,16
A	----- -/--	18

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	BIGI, FRANCA ET AL: "Heterogeneous enantioselective epoxidation of olefins catalysed by unsymmetrical (salen)Mn(III) complexes supported on amorphous or MCM-41 silica through a new triazine-based linker" CHEMICAL COMMUNICATIONS (CAMBRIDGE, UNITED KINGDOM) (2002), (7), 716-717, 21 March 2002 (2002-03-21), XP002265073 the whole document	1,4-6,8, 9,15,16
A	ALLEN ANNIS D ET AL: "POLYMER-SUPPORTED CHIRAL CO(SALEN) COMPLEXES: SYNTHETIC APPLICATIONS AND MECHANISTIC INVESTIGATIONS IN THE HYDROLYTIC KINETIC RESOLUTION OF TERMINAL EPOXIDES" JOURNAL OF THE CHEMICAL SOCIETY, CHEMICAL SOCIETY, LONDON, GB, vol. 121, no. 17, 1999, pages 4147-4154, XP001019176 ISSN: 0368-1769 the whole document	1,4-6,8, 10,15,16
A	ADIMA A ET AL: "CHIRAL ORGANIC-INORGANIC SOLIDS AS ENANTIOSELECTIVE CATALYTIC MATERIALS" JOURNAL OF MATERIALS CHEMISTRY, THE ROYAL SOCIETY OF CHEMISTRY, CAMBRIDGE, GB, vol. 7, no. 12, 1 December 1997 (1997-12-01), pages 2331-2333, XP000736603 ISSN: 0959-9428 the whole document	1,3,5,6, 8,11,15, 16,18
A	WO 01/044153 A (FACHE ERIC ;RHODIA POLYAMIDE INTERMEDIATES (FR); CLARK JAMES (GB);) 21 June 2001 (2001-06-21) claims	1,8,9,15
A	FERRAND A ET AL: "Hydrophilic diamine ligands for catalytic asymmetric hydrogenation of C=O bonds" TETRAHEDRON: ASYMMETRY, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, NL, vol. 13, no. 13, 19 July 2002 (2002-07-19), pages 1379-1384, XP004374310 ISSN: 0957-4166 the whole document	
A	"Organic Reactions vol. IV" 1948, WILEY, NEW YORK US, XP009023049 Chapter 5, IDE W S; BUCK J S: The Synthesis of Benzoin, pages 269-304 page 272 - page 277; table II	14
	-/--	

## INTERNATIONAL SEARCH REPORT

International Application No

PC., -- 03/03306

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; LI, TING-YOU ET AL: "Studies on the stereoselectivity of pinacol coupling reaction mediated by TiCl<sub>4</sub>-Mg" XP002265075 retrieved from STN Database accession no. 134:193158 structures abstract &amp; GAODENG XUEXIAO HUAXUE XUEBAO (2000), 21(9), 1391-1394,</p> <p>-----</p>	
A	<p>DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; SCHNEIDER, HANS JOERG ET AL: "1,2- Diphenyl - 1, 2 - diaminoethane derivatives as scissors shaped allosteric receptors" XP002265076 retrieved from STN Database accession no. 117:7579 abstract &amp; JOURNAL OF THE CHEMICAL SOCIETY, CHEMICAL COMMUNICATIONS (1992), (6), 490-1,</p> <p>-----</p>	
A	<p>DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; OGRETIR, CEMIL ET AL: "Reaction of 3,4-diethyl-2,5-dimethylpyrrole with 1,2-(substituted) diphenyl - 1, 2 - diaminoethanes" XP002265077 retrieved from STN Database accession no. 129:175629 structures abstract &amp; TURKISH JOURNAL OF CHEMISTRY (1998), 22(2), 137-142,</p> <p>-----</p>	
A	<p>KARL, JOHANN ET AL: "Ring-substituted [1,2-bis(4-hydroxyphenyl)ethylenediamine]d ichloropl atinum(II) complexes: compounds with a selective effect on the hormone-dependent mammary carcinoma" JOURNAL OF MEDICINAL CHEMISTRY (1988), 31(1), 72-83, XP002265074 table III Scheme III</p> <p>-----</p>	

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/GB 03/03306

## Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:  
1, 3-11 (in part); 15-18 (in part)

### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

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FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

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Continuation of Box I.2

Claims Nos.: -

Present claims 1-18 relate to an extremely large number of possible compounds/products/methods/uses. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the compounds/products/methods/uses claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. This is fundamental problem is further exacerbated by a lack of clarity within the meaning of Article 6 PCT in some of the aforementioned claims due to insufficient, inconsistent or no definition of technical features (e.g. features not within the scope of the independent claims defined in thereupon dependent claims, see claims 6, 7 and 13; no definition for the remaining imine, sulphonyl or urethane carbon moieties in independent claims 1, 12 and 15; generic "metal compound" in claim 15; vaguely defined uses in claim 18).

Consequently, the search has been carried out for those parts of the claims which appear to be sufficiently clear, supported and disclosed for the purposes of a meaningful search, at least by reference to common general knowledge either cited in the application (cf. page 1) or otherwise deemed apparent to the person skilled in the respective art, namely:

- claims 1, 12, 15: as is, **\*\*except\*\***: **\*\*linker group\*\*** embodiments of claims 6, 7 and 13 included; **\*\*imino-carbon moiety\*\*** as defined on page 3, lines 8-17; a **\*\*covalent\*\*** bond must be formed by the reaction of the "functional group" on the ligand and the "site capable of reacting with said functional group"; **\*\*metals\*\*** in claim 15 restricted to Fe, Co, Ni, Ru, Pd, Pt, Cu, Cr, Mn, Al;

- claim 14: as is, **\*\*except\*\*** step (d), restricted to **\*\*covalent\*\*** immobilisation, including optional embodiments immobilisation reaction via **\*\*interconversion\*\*** of the original functional group to give a suitable functional group and/or reaction with a polyethylene glycol derived **\*\*linker group\*\*** precursor to give a linker-modified ligand, as outlined on description pages 4, lines 4-8; 5, lines 5-10; 6, line 1 to page 7, line 8;

- claim 18: uses **\*\*restricted to\*\*** (i) (transfer) hydrogenation reactions, including carbonyl reductions with hydrogen; (ii) hydrolysis reactions, **\*\*further restricted to\*\*** hydrolytic kinetic resolution of epoxides; (iia) ring opening reactions, **\*\*further restricted to\*\*** epoxides; (iii) carbon-carbon bond forming reactions, **\*\*further restricted to\*\*** Heck reactions and Suzuki reactions; (iv) epoxidations;

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FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

(v) aziridinations; (vi) hetero Diels-Alder reactions.

with the corresponding restrictions in the therefrom dependent claims.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.5), should the problems which led to the Article 17(2) declaration be overcome.

# INTERNATIONAL SEARCH REPORT

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FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1, 3-11 (in part); 15-18 (in part)

insofar as relating to an immobilised 1,2-ethylenediamine derived ligand (IV) obtainable by reaction of a compound of formula (I), or a **\*\*generic linker\*\***-modified derivative (I') of such a compound, obtainable by prior reaction with a linker molecule that provides a functional group capable of reaction with the solid support, with a solid support having a suitable reactive site to form a covalent bond, the ligand (IV) being one of the above defined reaction products with **\*\*either\*\*** (IV-b) a compound of formula (I), which **\*\*does not\*\*** have a functionalised aryl substituent at at least one of the R1-R4 positions, or (IV-b') a said derivative (I') thereof; an immobilised catalyst (V-b) comprising (IV-b) or (IV-b') and a metal compound of Fe, Co, Ni, Ru, Pd, Pt, Cu, Cr, Mn or Al; the use of catalyst (V-b) for performing **\*\* (transfer) hydrogenation reactions\*\***, including carbonyl reductions with hydrogen.

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2. claim: 18 (in part)

insofar as relating to the use of catalyst (V-b) for performing **\*\*hydrolytic kinetic resolution of epoxides\*\*** or **\*\*ring opening reactions of epoxides\*\***.

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3. claim: 18 (in part)

insofar as relating to the use of catalyst (V-b) for performing carbon-carbon bond forming reactions selected from **\*\*Heck reactions and Suzuki reactions\*\***.

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4. claim: 18 (in part)

insofar as relating to the use of catalyst (V-b) for performing **\*\*epoxidations\*\***.

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5. claim: 18 (in part)

insofar as relating to the use of catalyst (V-b) for performing **\*\*aziridinations\*\***.

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6. claim: 18 (in part)

insofar as relating to the use of catalyst (V-b) for performing **\*\*hetero Diels-Alder reactions\*\***.

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FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

## 7. claims: 1-18 (in part)

insofar as concerning an immobilised 1,2-ethylenediamine derived ligand (IV) obtainable by reaction of a compound of formula (I), or a \*\*generic linker\*\*-modified derivative (I') of such a compound, obtainable by prior reaction with a linker molecule that provides a functional group capable of reaction with the solid support, with a solid support having a suitable reactive site to form a covalent bond, the ligand (IV) being one of the above defined reaction products with \*\*either\*\* (IV-a(i)) a compound of formula (I) with a functionalised \*\*aryl\*\* substituent at at least one of the R1-R4 positions, (IV-a(i)') a said derivative (I') thereof the use of \*\*catalyst (V-a)\*\* for performing (transfer) hydrogenation reactions, including carbonyl reductions with hydrogen, hydrolytic kinetic resolution of epoxides, ring opening reactions of epoxides, carbon-carbon bond forming reactions selected from Heck reactions and Suzuki reactions, epoxidations, aziridinations, hetero Diels-Alder reactions.

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## 8. claims: 12, 13 (whole)

concerning a linker-modified ligand (III-a(ii)'), i.e. an embodiment of a possible starting material for the preparation of (IV-a(i)'), with \*\*specified linker groups\*\*, selected from (III-a(ii)-1') the ensemble of those defined in claim 12 by way of the \*\*separate listing of linking and spacing moieties in the precursor compounds giving the linker groups\*\* upon reaction with free ligand (III-a(ii)) and (III-a(ii)-2') a polyethylene glycol derived linker group.

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## 9. claim: 14 (in part)

insofar as relating to a benzoin condensation of a functionalized benzaldehyde to give a functionalised benzoin \*\*intermediate product (I-a(iii))\*\*, as defined in step (a).

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## 10. claim: 14 (in part)

insofar as relating to a reduction of (I-a(iii)) to give a functionalised hydrobenzoin \*\*intermediate product (II-a(iii))\*\*, as defined in step (b).

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## 11. claim: 14 (in part)

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FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

insofar as relating to transforming (II-a(iii)), preferably via reaction with TsCl to give the \*\*ditosylate intermediate product\*\* and subsequently with NaN<sub>3</sub> to give the \*\*diazide intermediate product\*\* and subsequently with LiAlH<sub>4</sub>, to give a functionalised 1,2-diarylethylenediamine \*\*intermediate product (III-a(iii))\*\*, as defined in step (c).

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP03/03306

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 0144153 . A	21-06-2001	FR 2802526 A1	22-06-2001
		BR 0016440 A	01-10-2002
		CA 2394259 A1	21-06-2001
		CN 1414937 T	30-04-2003
		EP 1237836 A1	11-09-2002
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		US 2003097025 A1	22-05-2003
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